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3,8-Di-*C*-arabinosylluteolin, a new flavonoid from *Pteris vittata*.—In spite of the fact that fern flavonoids are of chemotaxonomic interest, little is known of the distribution of these compounds in some fern families (e.g. Pteridaceae). Previous work on the flavonoids of *Pteris vittata* L. (Pteridaceae) has led to the identification of an anthocyanin (luteolinidin 5-*O*-glucoside) by Harborne (Phytochemistry 5:589–600, 1966). In addition, acid hydrolysis of extracts of this fern has led to the identification of kaempferol, quercetin, leucocyanidin and leucodelphinidin by Voirin (Ph. D. thesis, University of Lyon, p. 151, 1970). More recently 3-*C*-(6‴-acetyl-cellobiosyl)-apigenin (Amer. Fern J. 89:217–220, 1999) and 6-*C*-cellobiosylisoscutellarein 8-methyl ether together with quercetin 3-*O*-glucuronide and rutin (Amer. Fern J. 90:42–47, 2000) have been identified by Imperato and Telesca. Three kaemperol glycosides (3-*O*-glucoside, 3-*O*-glucuronide and 3-*O*-(X″,X″-di-protocatechuoyl)-glucuronide) together with quercetin 3-*O*-(X″,X″-di-protocatechuoyl)-glucuronide have been found in this fern by Imperato (Amer. Fern J. 90: 141–144, 2000).

In the present paper a new *C*-glycosylflavone (identified as 3,8-di-*C*-arabinosyl-luteolin (I)) and 6-*C*-arabinosyl-8-*C*-glucosylluteolin (II) have been isolated from *Pteris vittata* L. growing in the Botanic Garden of the University of Naples. This fern has been identified by Dr. R. Nazzaro (University of Naples); a voucher specimen (149.001.001.01) has been deposited in the Herbarium Neapolitanum (NAP) of the University of Naples.

Flavonoids (I and II) were isolated from an ethanolic extract of aerial parts of *Pteris vittata* L. by preparative paper chromatography in BAW (*n*-butanol-acetic acid-water, 4:1:5, upper phase), 15% HOAc (acetic acid) and BEW (*n*-butanol-ethanol water, 4:1:2.2). Further purification was carried out by Sephadex LH-20 column chromatography eluting with methanol.

Color reactions (brown to yellow in UV+NH_3), ultraviolet spectral analysis in the presence of usual shift reagents (λ_{max} (nm) (MeOH) 258, 272, 348; +NaOAc 283, 322 (sh), 402; +NaOMe 266, 281, 340 (sh), 407 (increase in intensity); +$AlCl_3$ 277, 299 (sh), 331 (sh), 426; +$AlCl_3$/HCl 280, 300 (sh), 358, 388) and chromatographic behaviour (R_f values on Whatman No 1 paper: 0.15 in BAW; 0.31 in 15% HOAc; 0.12 in H_2O) suggested that flavonoid (I) may be a flavonoid glycoside with free hydroxyl groups at positions 5, 7, 3′ and 4′. Since treatment with 2N HCl (2 hr at 100°C) failed to produce an aglycone, flavonoid (I) may be a *C*-glycosylflavonoid. Electrospray mass spectrum (ESMS) showed a pseudomolecular ion at m/z 573 $[(M+H)+Na]^+$, an ion at m/z 595 $[(M+H)+2\ Na]^+$ and an ion at m/z 1123 $[(M \times 2)+ Na+H]^+$ which corresponds to a dimer. These data suggest that flavonoid (I) is a di-*C*-pentosylluteolin. ^1H NMR spectrum (DMSO-d_6) showed signals at δ 3.11–3.91 (ten sugar protons, m), δ 4.61 (1H, d, J=8 Hz, anomeric proton), δ 4.68 (1H, d, J=8 Hz, anomeric proton), δ 6.27 (1H, s, H-6), δ 6.93 (1H, d, J=8.8

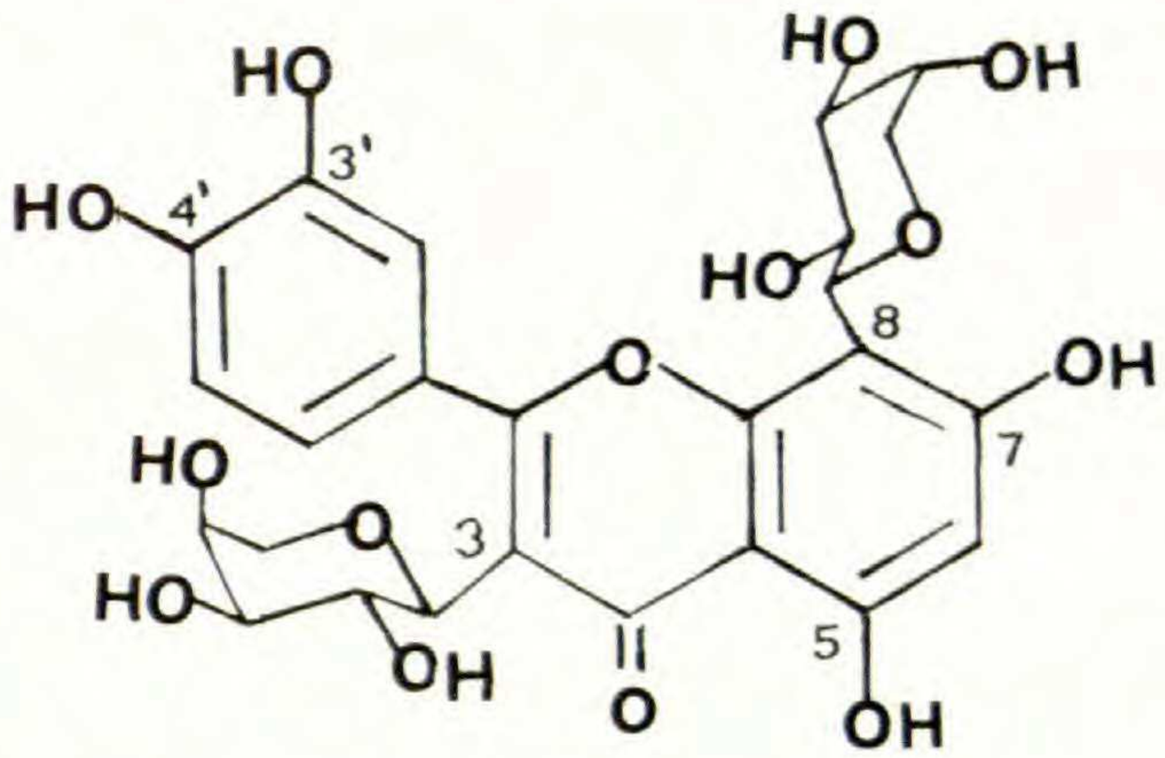

FIG. 1.

Hz, H-5′), δ 7.39 (1H, dd, J=2.0 and 8.8 Hz, H-6′) and δ 7.40 (1H, d, J=2 Hz, H-2′). These data suggest that flavonoid (I) is a luteolin 3,8-di-*C*-pentoside.

Wessely-Moser isomerization (3N HCl; 3 hr at 100°C) gave a mixture in which flavonoid (I) and four isomers were detected by paper chromatography in BAW; these isomers were not present in sufficient amount to allow characterization. ^{1}H NMR spectrum (DMSO-d_6) of the above mixture showed a singlet at δ 6.56 (H-8) and a singlet at δ 6.26 (H-6) confirming that flavonoid (I) is a 3,8-di-*C*-glycosylflavone. Since flavonoid (I) gave at least four isomers, arabinose may be attached at C-3 and/or C-8 because *C*-arabinosylflavones on acid treatment undergo pyranose-furanose isomerization and α-linkage-β-linkage isomerizatiion of *C*-glycosidic link as described in a review of Chopin et al. (pp. 449–503 *in* J.B. Harborne and T. J. Mabry eds., *The Flavonoids: Advances in Research*, Chapman and Hall, London, New York, 1982). Treatment of flavonoid (I) with 2,2-dimethoxypropane and 6N HCl-dioxan in dry dimethylformamide according to Jarman and Ross (J. Chem. Soc. (C):199–203, 1969) gave a diisopropilidene derivative ($[M]^+$ at m/z 630 in EI-mass spectrum); hence arabinose is attached at C-3 and C-8 of flavonoid (I) since this isopropilidenation is specific for *C*-galactosyl and *C*-arabinosyl residues in mono- and di-*C*-glycosylflavones as described in the above review by Chopin *et al.* $FeCl_3$ oxidation of flavonoid (I) gave L-arabinose. The above results show that flavonoid (I) is 3,8-di-*C*-arabinosylluteolin (Fig. 1), a new natural product; this is the first report of a 3,8-di-*C*-glycosylflavone from ferns.

3,8-Di-*C*-glycosylflavones were found for the first time in plants in 1985 by Matsubara et al. (Nippon Nogeikayaku Kaishi 59: 405–410, 1985) who isolated apigenin 3,8-di-*C*-glucoside and diosmetin 3,8-di-*C*-glucoside from *Citrus sudachi* peelings; subsequently these two flavonoids have been found also in *Citrus sinensis* peelings (Agric. Biol. Chem. 50: 781–783, 1986) and the former flavonoid has been found also in *Citrus junos* peelings (Nippon Nogeikayaku Kaishi 59: 683–687, 1985) by Kumamoto et al.

Flavonoid (II) was identified as luteolin 6-*C*-arabinoside-8-*C*-glucoside by ultraviolet spectral analysis with usual shift reagents, treatment with 2N HCl (which failed to give an aglycone), ESMS (which gave a pseudomolecular

ion at m/z 603 ($[(M+H)+Na]^+$), $FeCl_3$ oxidation (which gave D-glucose and L-arabinose) and ^1H NMR spectrum (DMSO-d_6). Assignment of D-glucose to C-8 was based on doublings of signals in ^1H NMR spectrum (two signals were observed for H-3 and H-6′) since this feature is due to the presence of a *C*-linked hexose at C-8 as described in a review by Jay (pp. 57–93, *in* J.B. Harborne ed., *The Flavonoids, Advances in Research since 1986*, Chapman and Hall, London, 1994). Flavonoid (II) is a new fern constituent; it has previously been found in bryophytes (*Blepharostoma tricophyllum* and *Pleurozia conchifolia*) and in angiosperms (*Lespedeza capitata*, *Glycine max* and *Astrantia major*) as described in the review by Jay.

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